Nanostructured, High Surface Area Materials for Sensing Applications

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CNMS User since 2006

Acknowledgements

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Theoretical calculations

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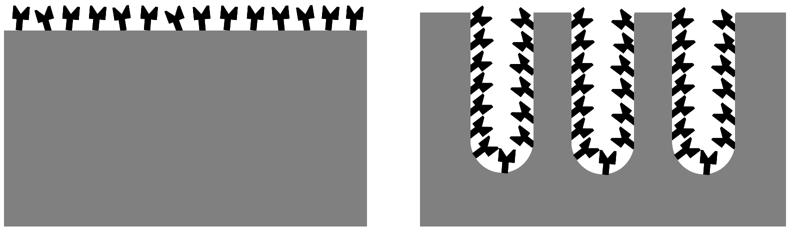
Outline

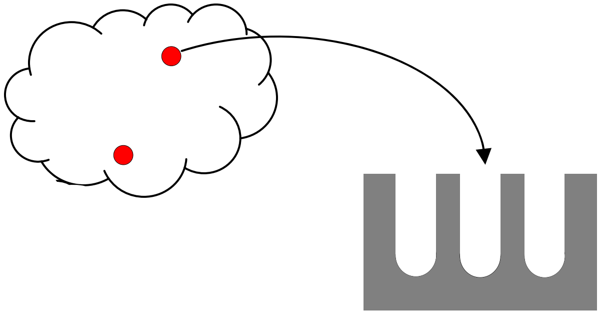
- Motivation: Nanoscale porous materials for sensing
- Porous silicon waveguide sensor
  - Importance of pore size
- Porous silicon diffraction grating sensor
  - DIPS process
- Dual mode sensing with porous silicon thin film
- Conclusions

Advantages of Nanoporous Materials

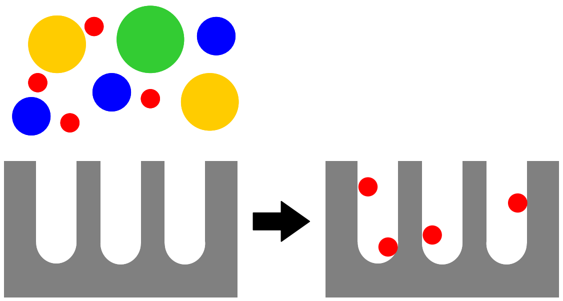
- Significantly increased surface area



- Preconcentration of molecules in active sensing region



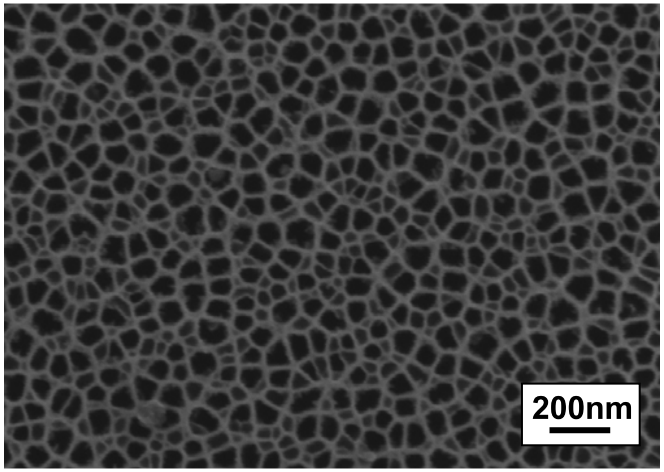
- Filtering of larger contaminant molecules



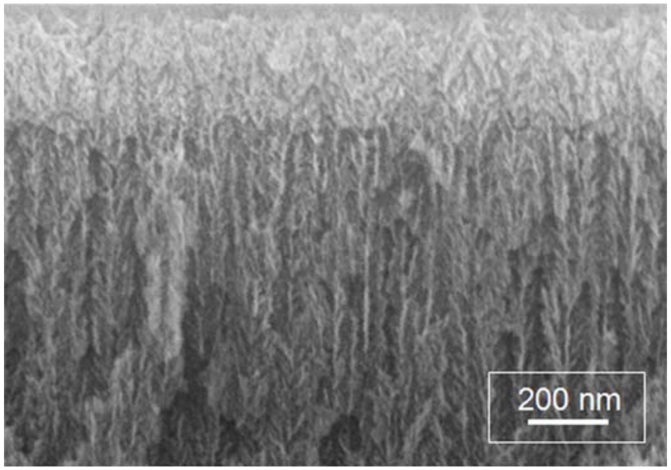
Our Approach: Porous Silicon

- Formed by electrochemical etching in HF-based electrolyte
- Tunable pore size between ~10-100 nm
  - Silicon substrate doping
- Tunable thickness between ~10 nm and wafer thickness
  - Etching time
- Tunable refractive index (porosity) between ~1.15 (90%) & 3.30 (30%)
  - Applied current density
- High quality optical structures can be fabricated (e.g., waveguides)

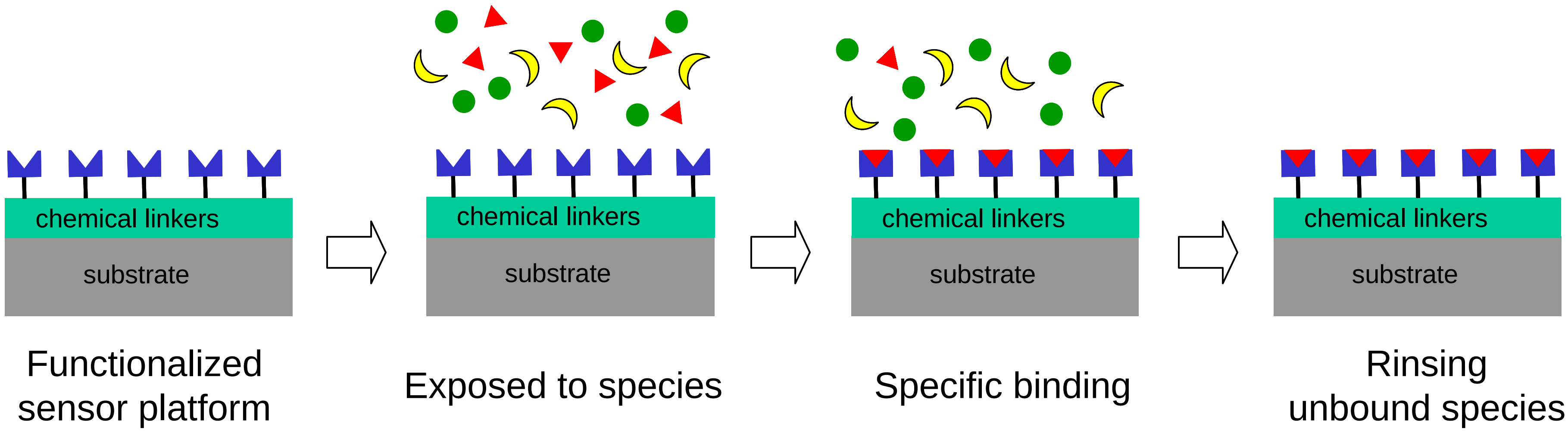
Top view



Cross-section



Basic Sensing Principle: Specific Binding



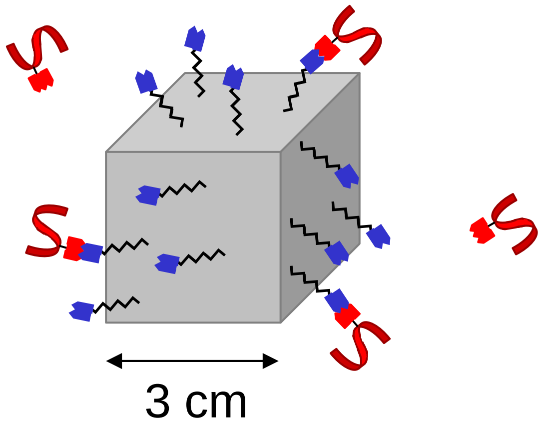
Label-free detection: molecular binding causes change in refractive index or absorption

Labeled detection: fluorophore tagged to target emits light upon excitation by optical field of sensor

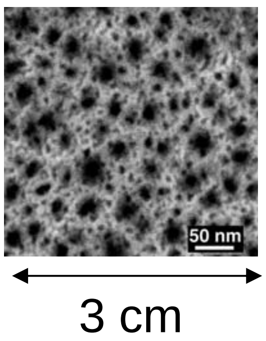
Porous Materials for Sensing

Surface area for molecular attachment and detection

Planar sensors



Porous sensors



Pores are especially advantageous for small molecule detection

54 cm^2

5400 m^2 !!!

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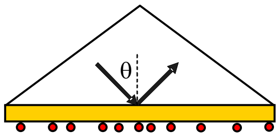
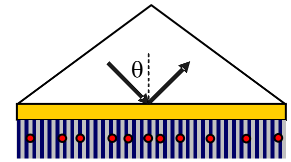
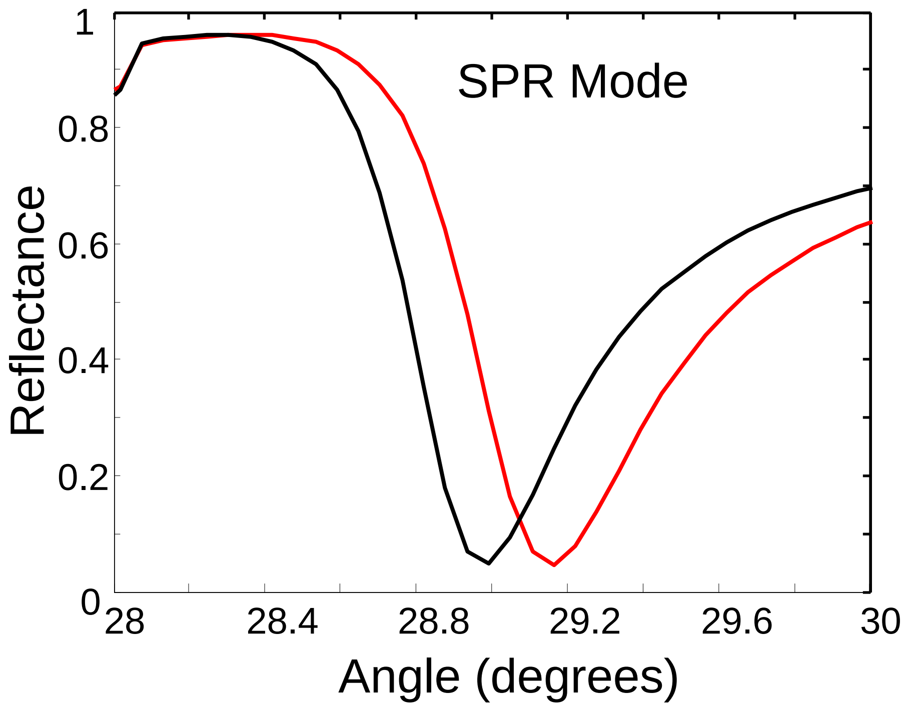
Interesting Comparison

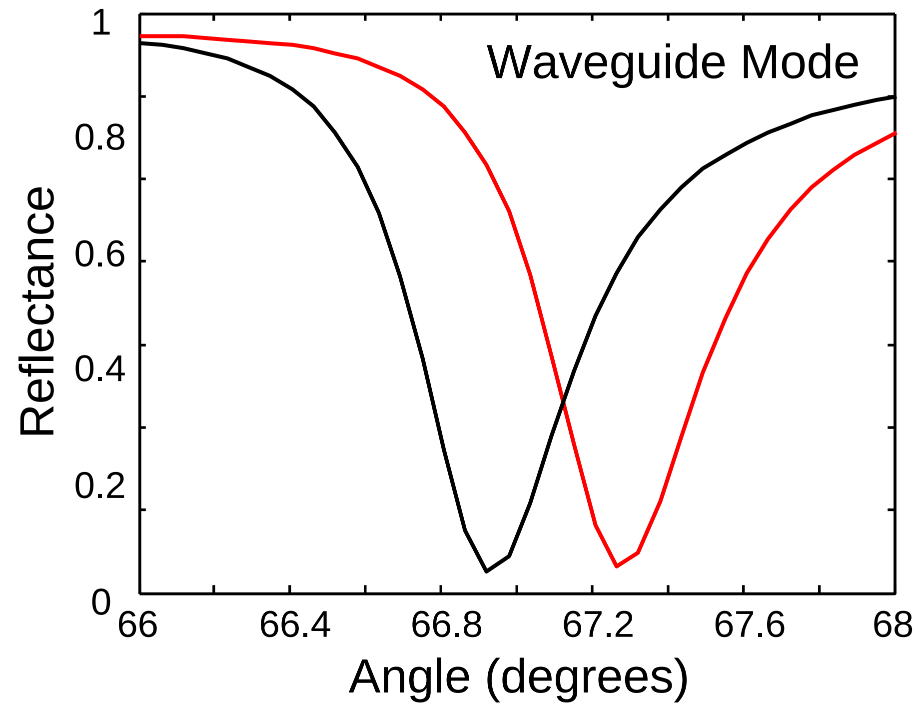


Traditional SPR…

+ porous layer





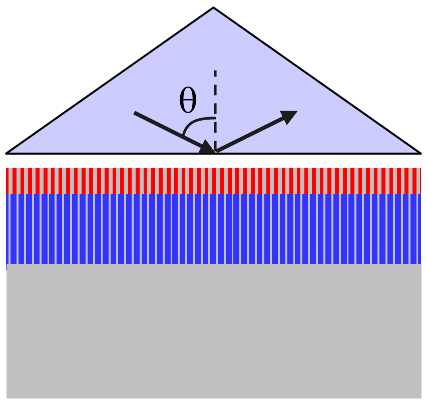


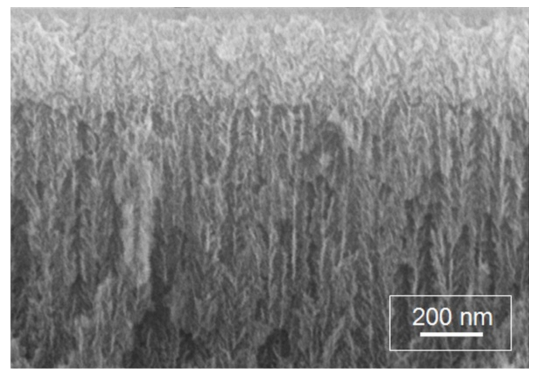
<u>For small molecule detection</u>

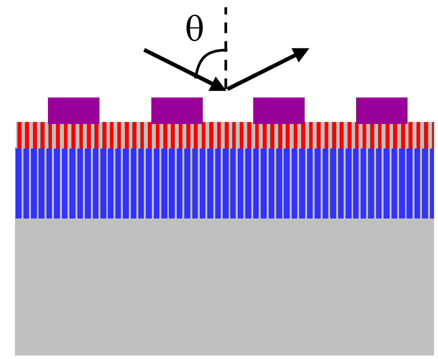
Traditional SPR confinement factor ~ 2%

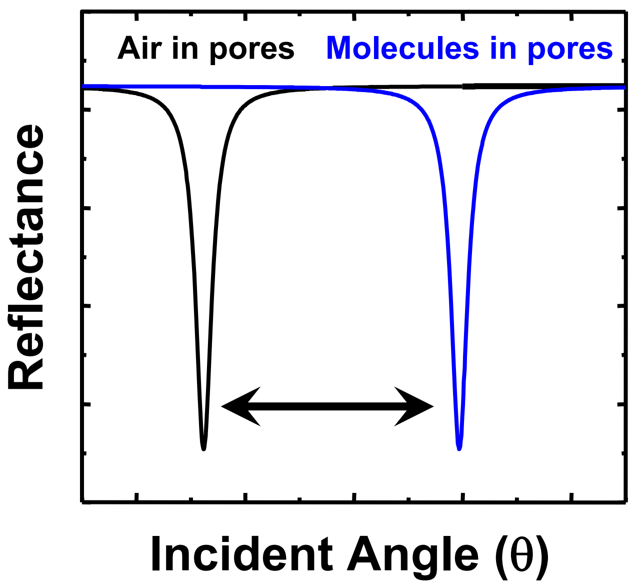
+ porous layer confinement factor ~ 97%

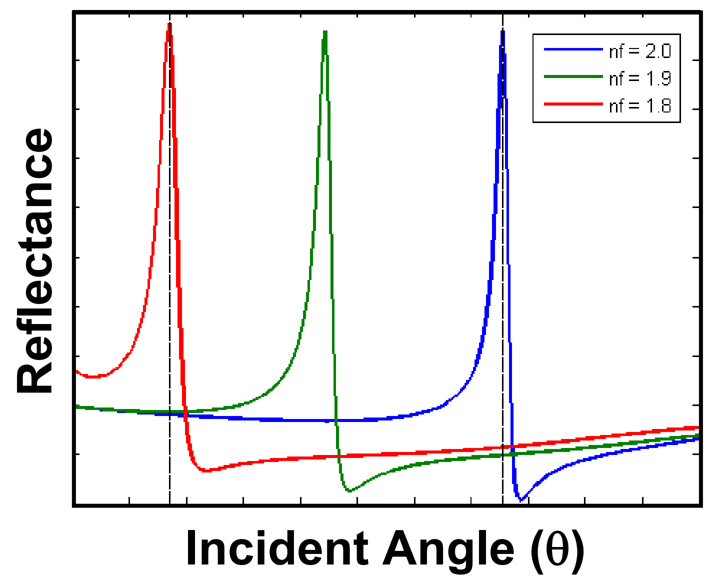
Measurement Approaches





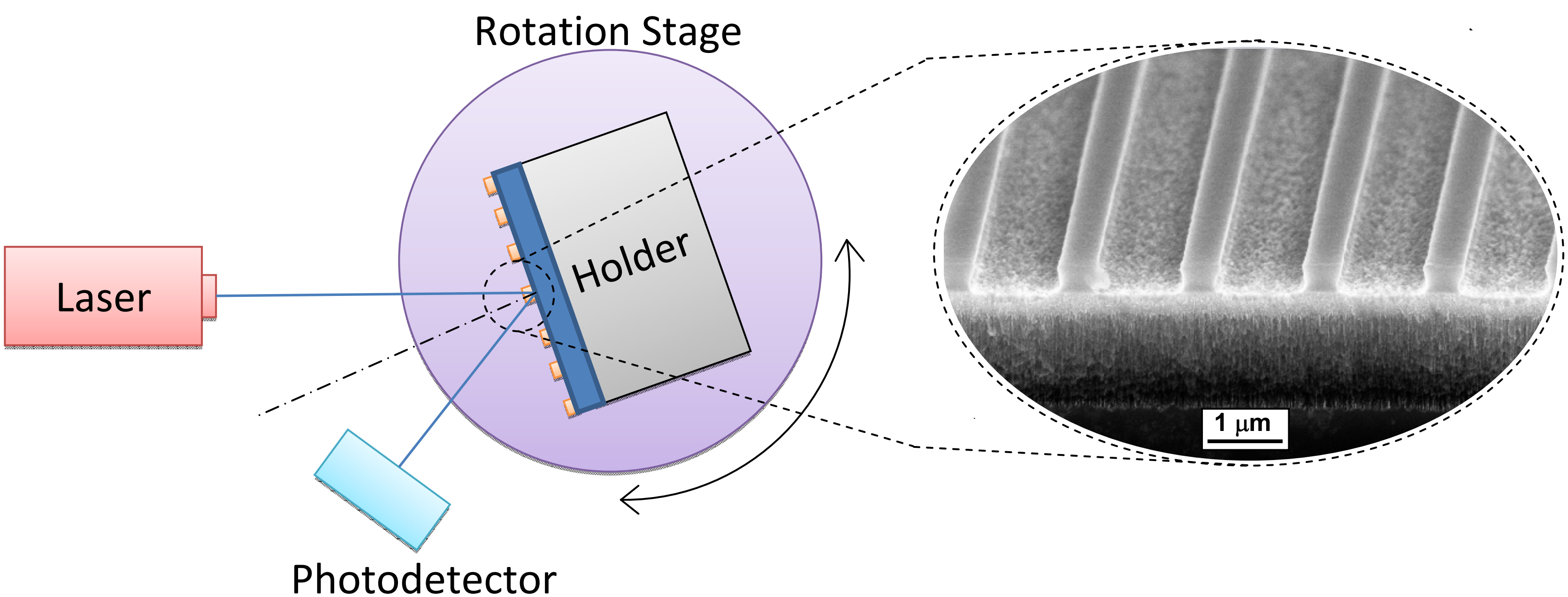






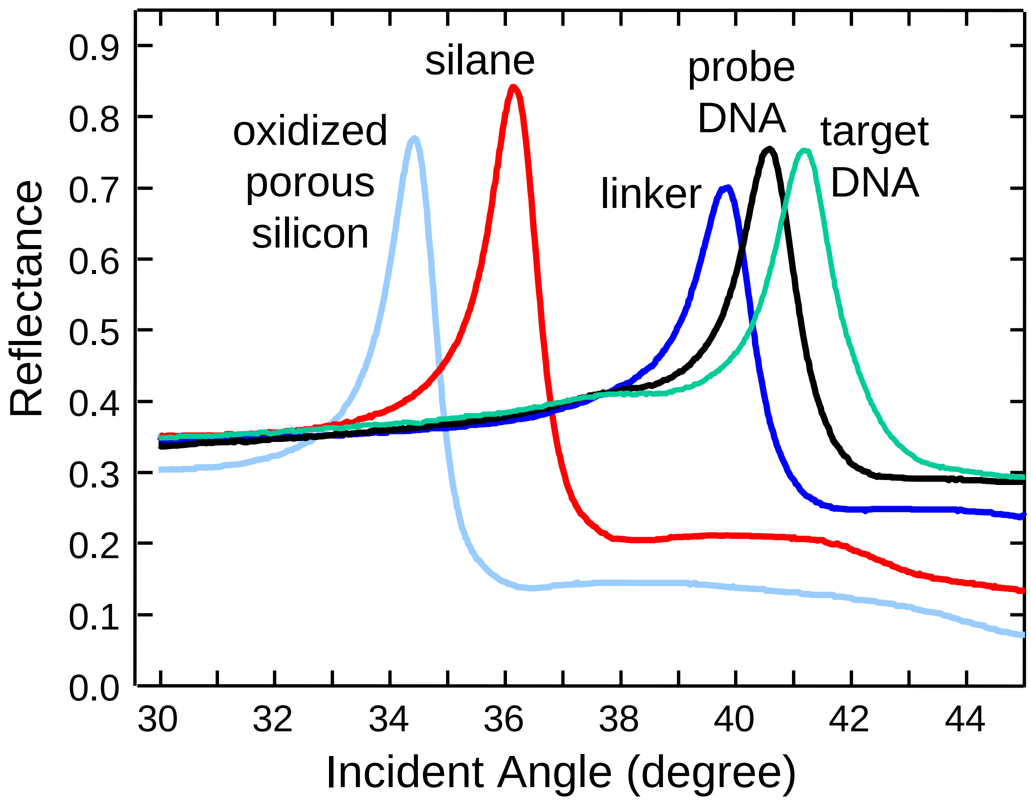
Porous Silicon Waveguide

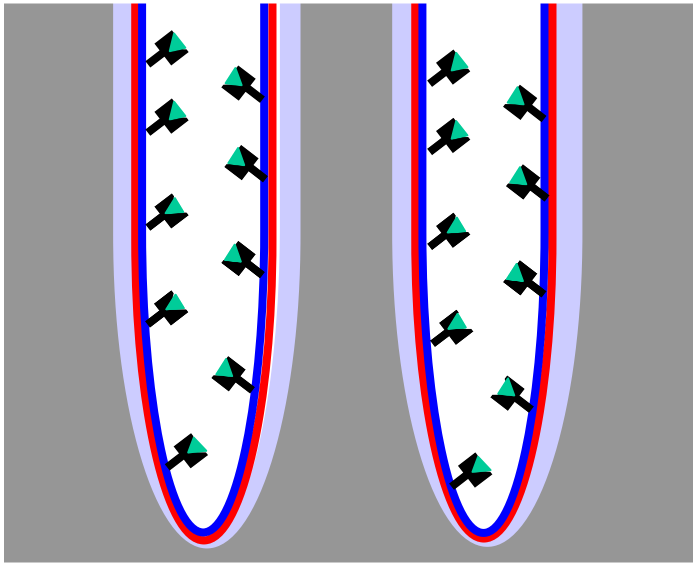
- Light couples into waveguide at discrete angle(s)
  - Angle depends on waveguide refractive index (variable) and grating period (fixed)
  - $\sin\theta = N_{eff} - \frac{\lambda}{\Lambda}$



****Gratings fabricated at CNMS****

PSi Waveguide: DNA Sensing





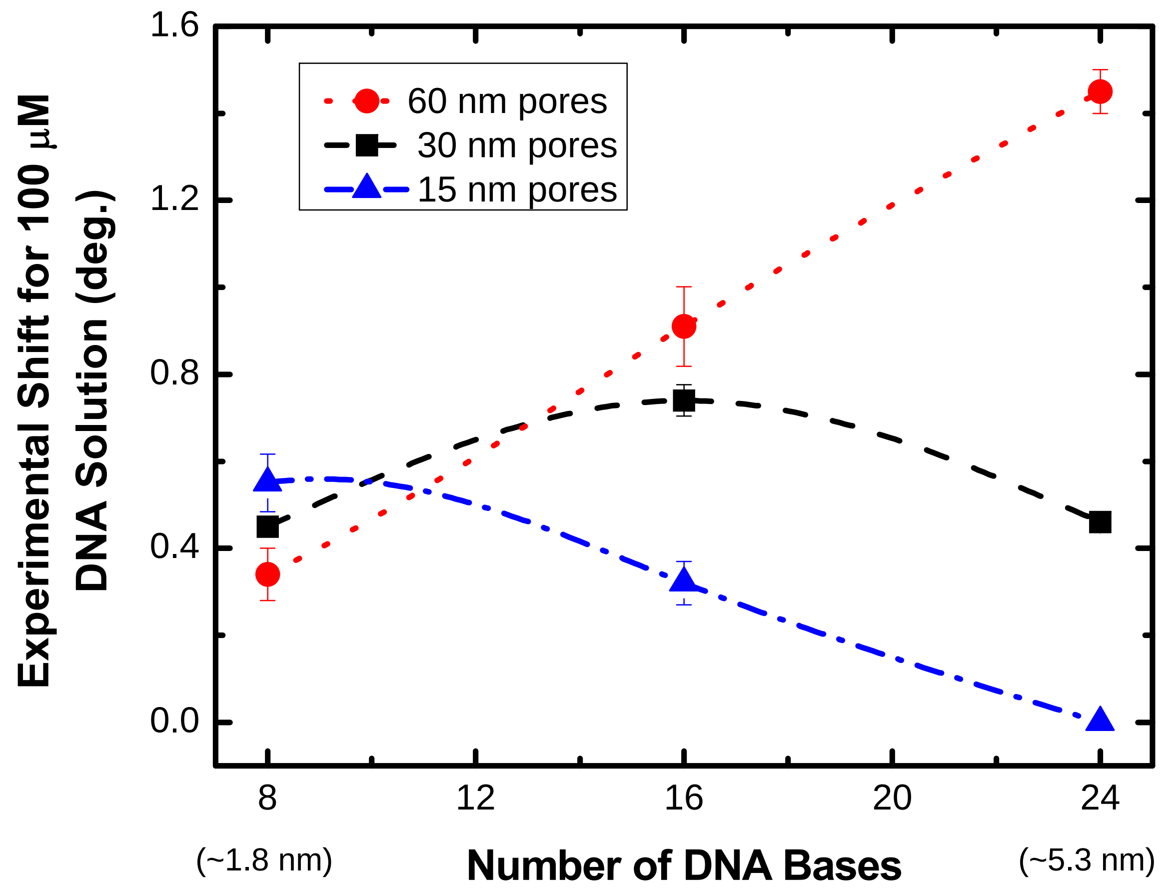
1. Thermal oxidation
2. Aminosilane (3-APTES)
3. Sulfo-SMCC
4. Probe DNA
5. Target DNA

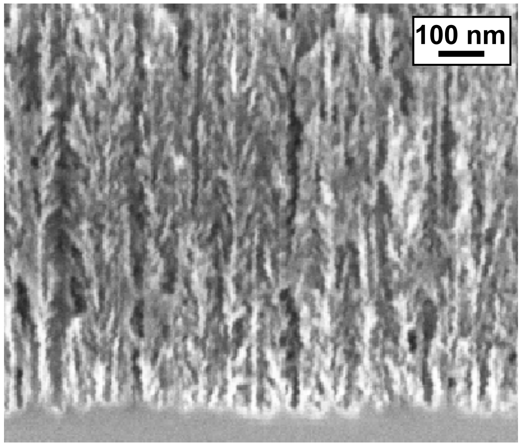
JAP **104**, 123113 (2008)

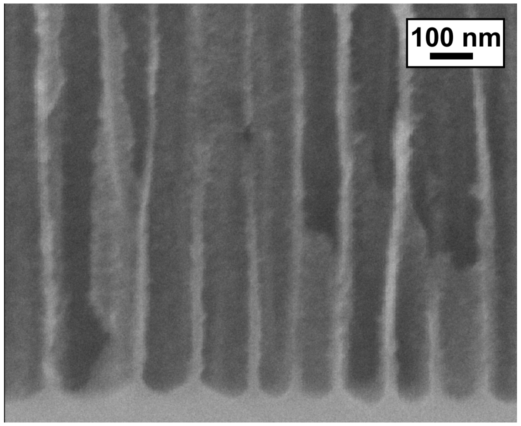
Biosens. Bioelectron. **23**, 1572 (2008)

Importance of Pore Size

Pore morphology and size play a significant role in small molecule detection







IEEE Trans. Nanotechnol. **9**, 596 (2010)

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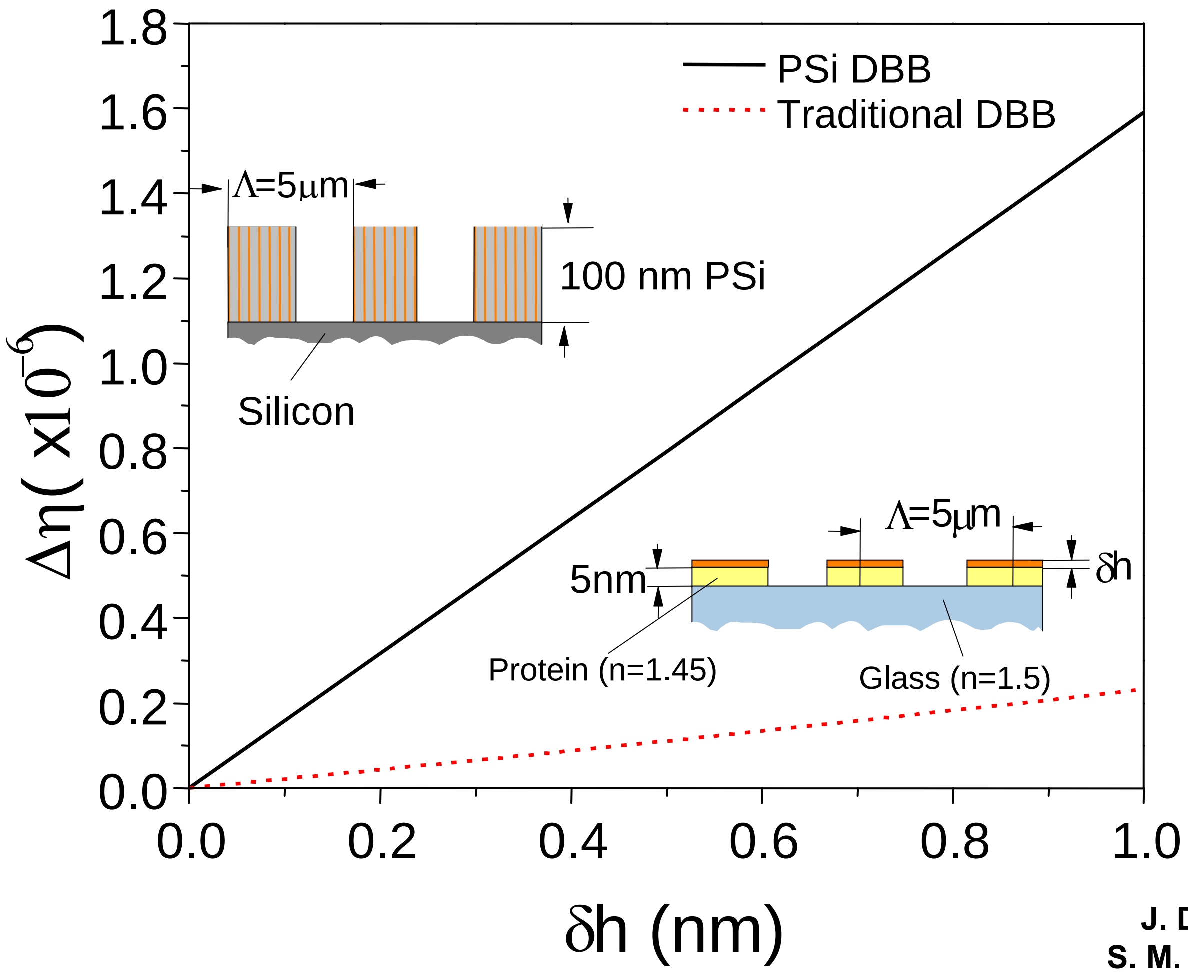
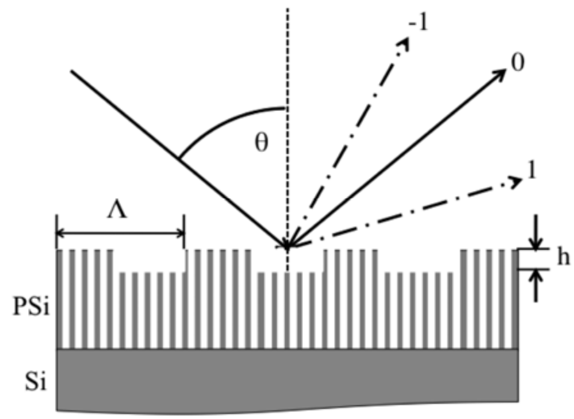
Diffraction-Based Biosensing

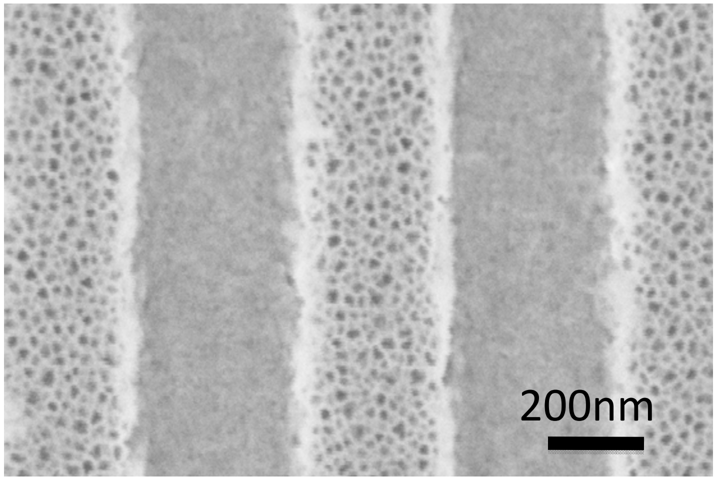
$$\eta = \alpha(f, \Lambda, \lambda, ..)(h\Delta n)^2$$

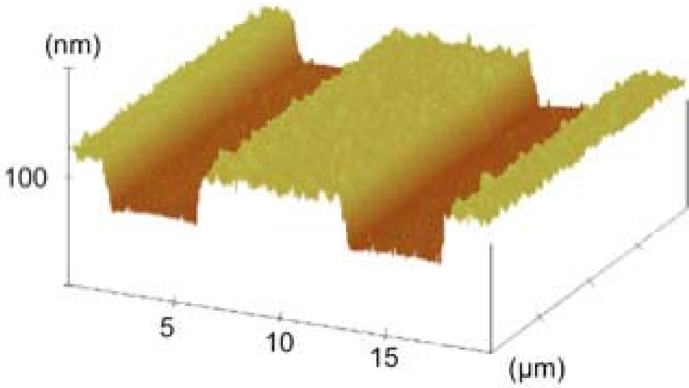


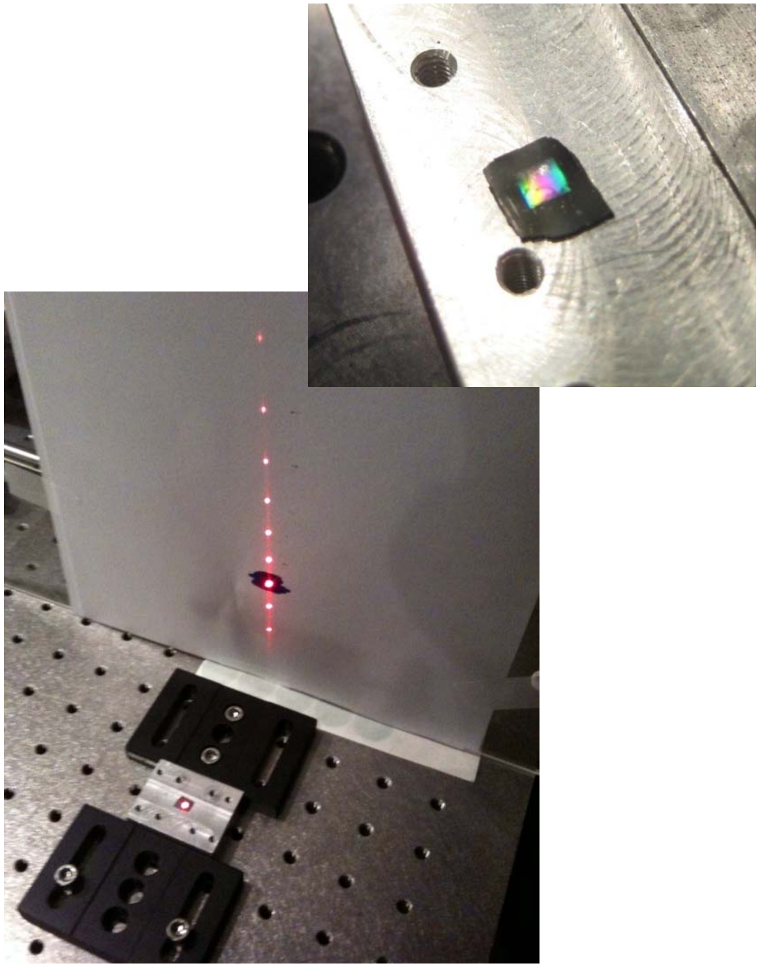


J. D. Ryckman, M. Liscidini, J. E. Sipe, and S. M. Weiss, Appl. Phys. Lett. 96, 171103 (2010)

Porous Silicon Diffraction Grating

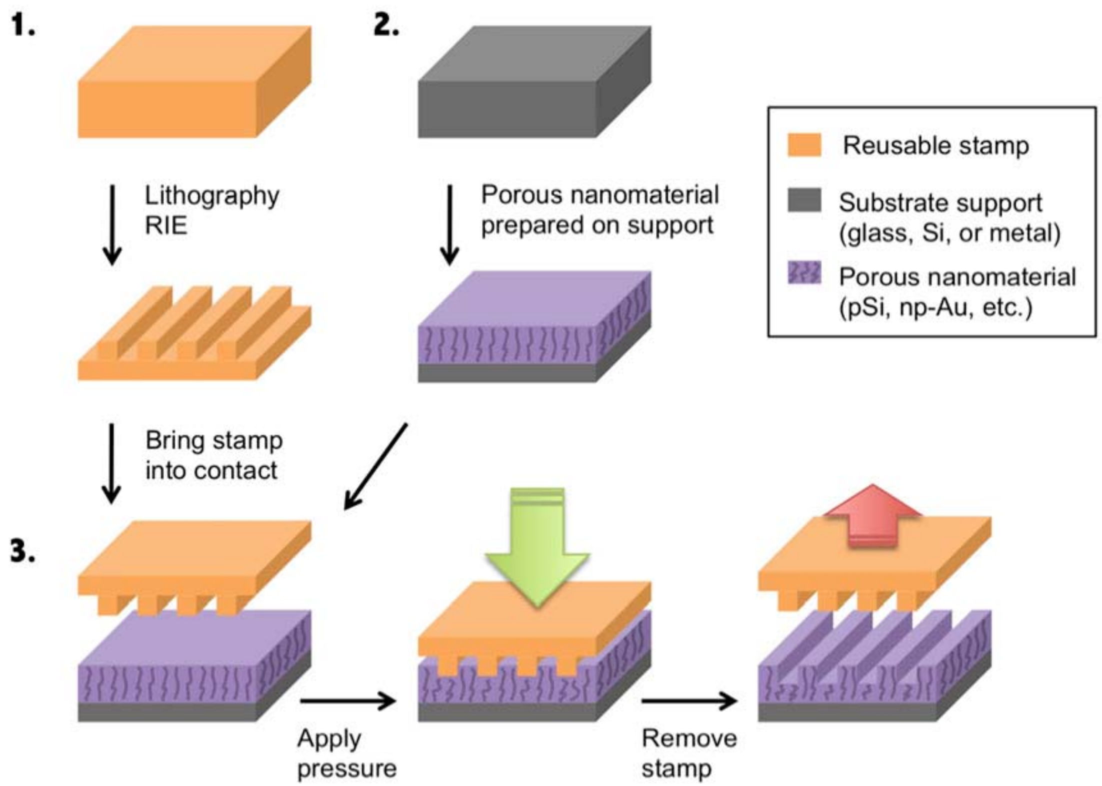


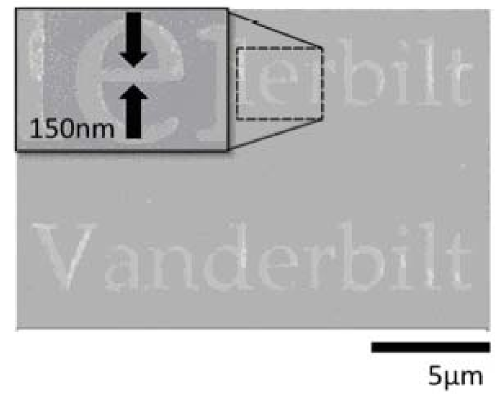


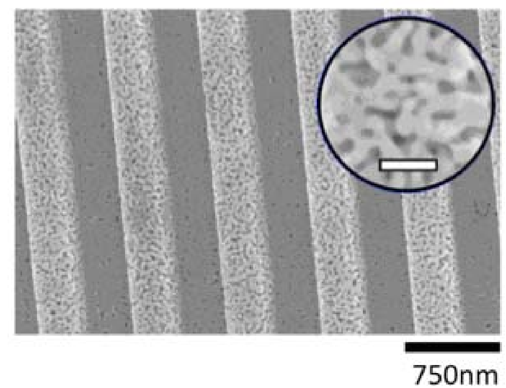


Fabrication: DIPS

Direct Imprinting of Porous Substrates





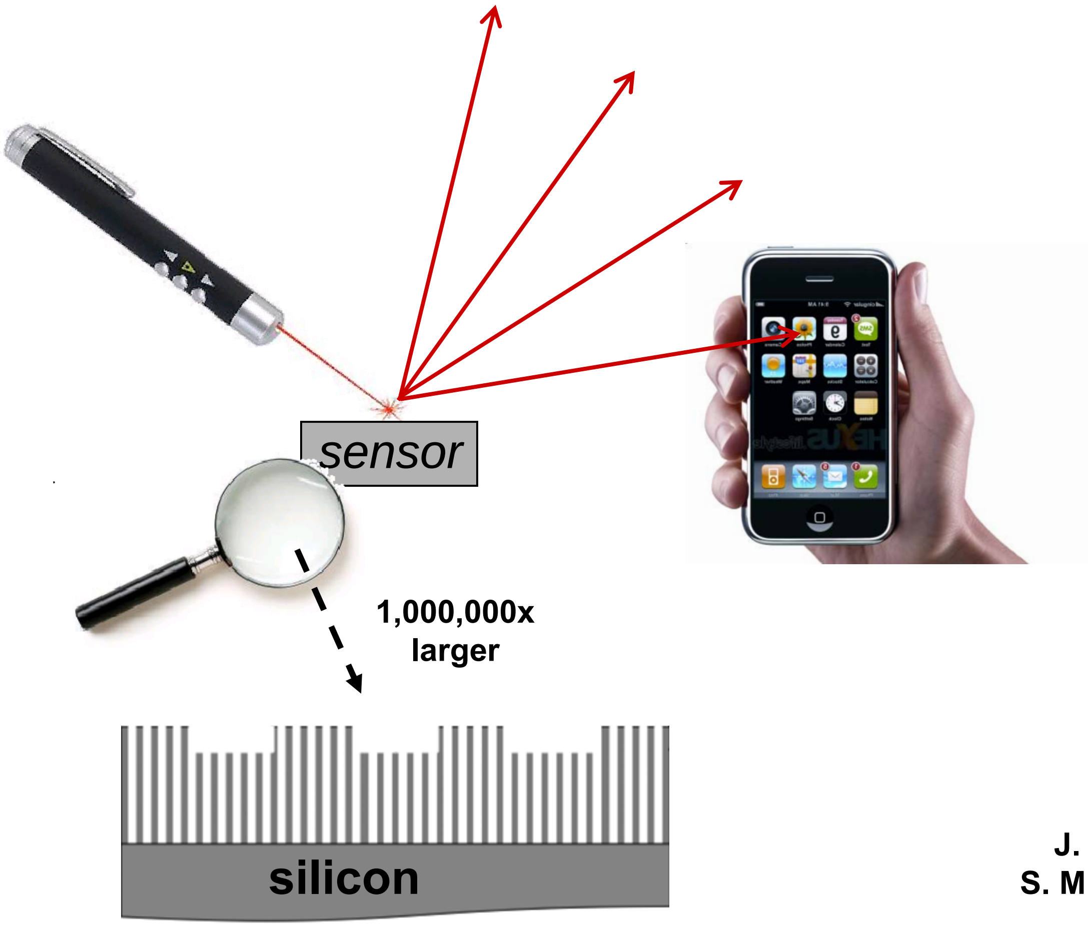


****Stamps fabricated at CNMS****

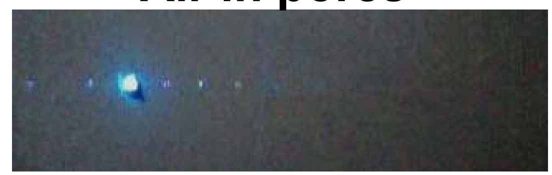
J. D. Ryckman, M. Liscidini, J. E. Sipe, and S. M. Weiss, "Direct Imprinting of Porous Substrates: A Rapid and Low-Cost Approach for Patterning Porous Nanomaterials," Nano Lett., in press. (Available online)

"Breath test"

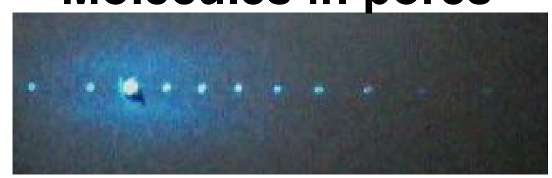
Increase diffraction efficiency when water vapor infiltrates porous silicon grating



Air in pores



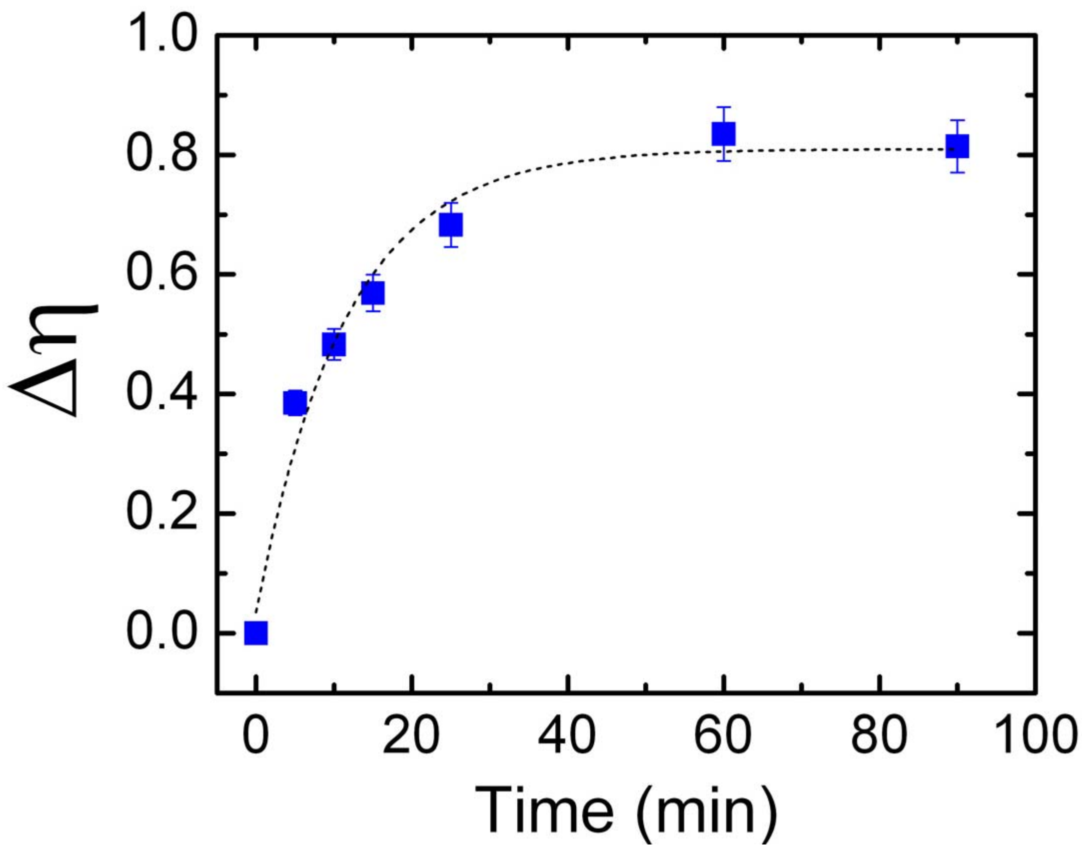
Molecules in pores



J. D. Ryckman, M. Liscidini, J. E. Sipe, and S. M. Weiss, Appl. Phys. Lett. 96, 171103 (2010)

Time Response of Molecule Attachment

Exposure to 0.25% 3-aminopropyltriethoxysilane (0.8 nm molecule)



Significantly faster monolayer formation results from exposure to even 1% 3-APTES solutions

J. D. Ryckman, M. Liscidini, J. E. Sipe, and S. M. Weiss, Appl. Phys. Lett. 96, 171103 (2010)

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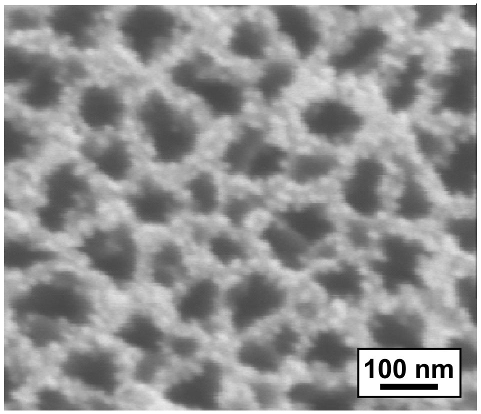
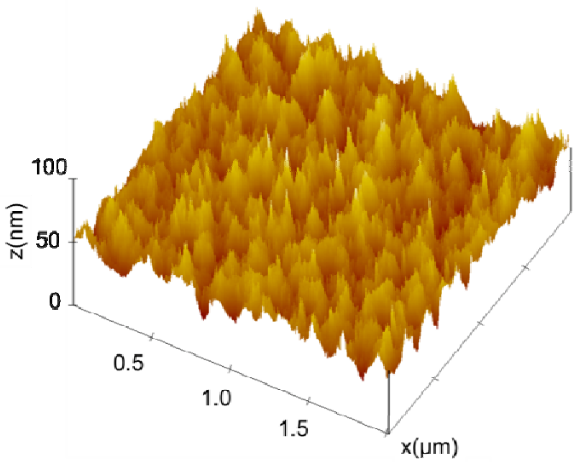
Porous Silicon Dual Mode Sensor

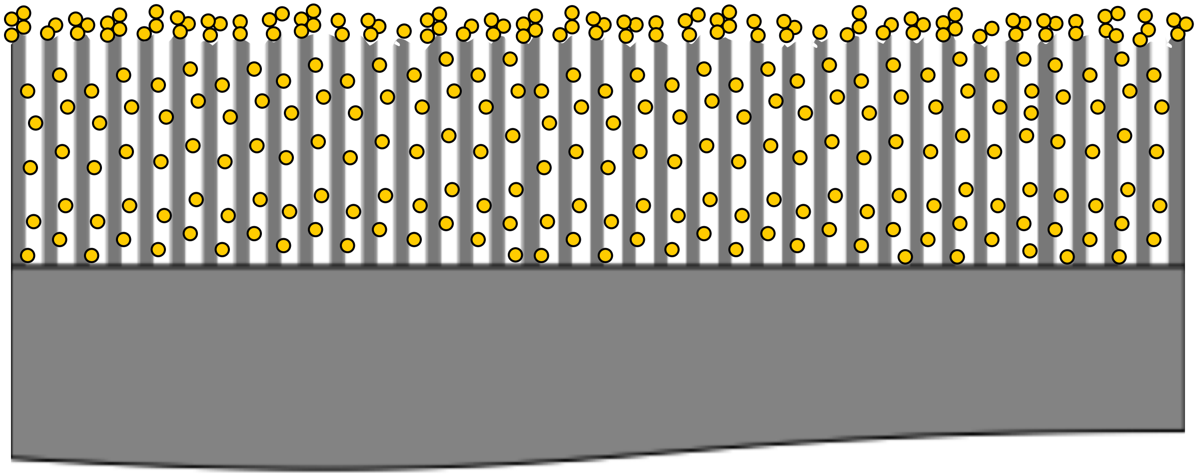


SERS

Refractive Index



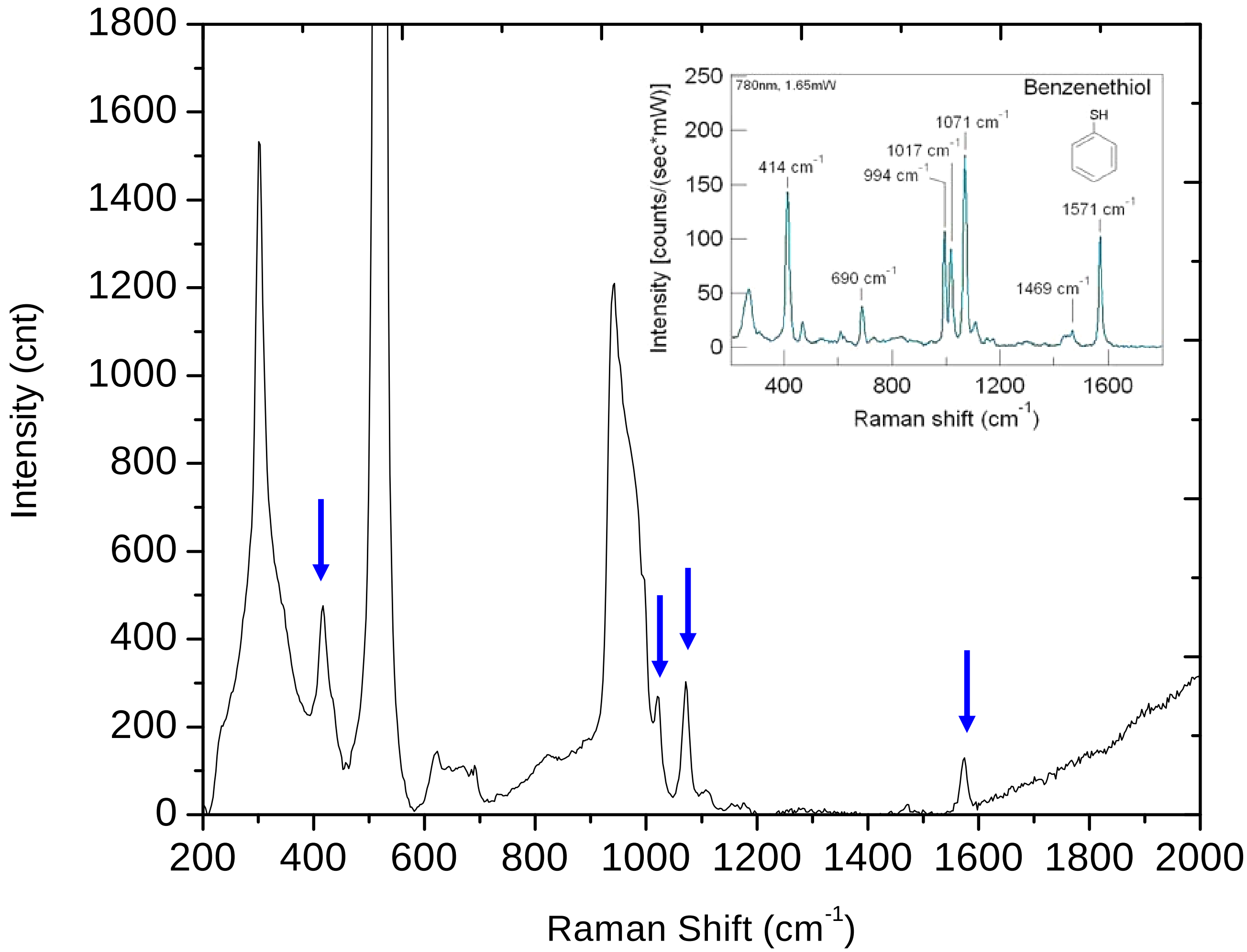
1. Etch PSi
2. Remove PSi to roughen top surface
3. Etch PSi
4. Infiltrate Au NPs



Y. Jiao, D. S. Koktysh, N. Phambu, and S. M. Weiss, "Dual-mode sensing platform based on colloidal gold functionalized porous silicon," manuscript in review.

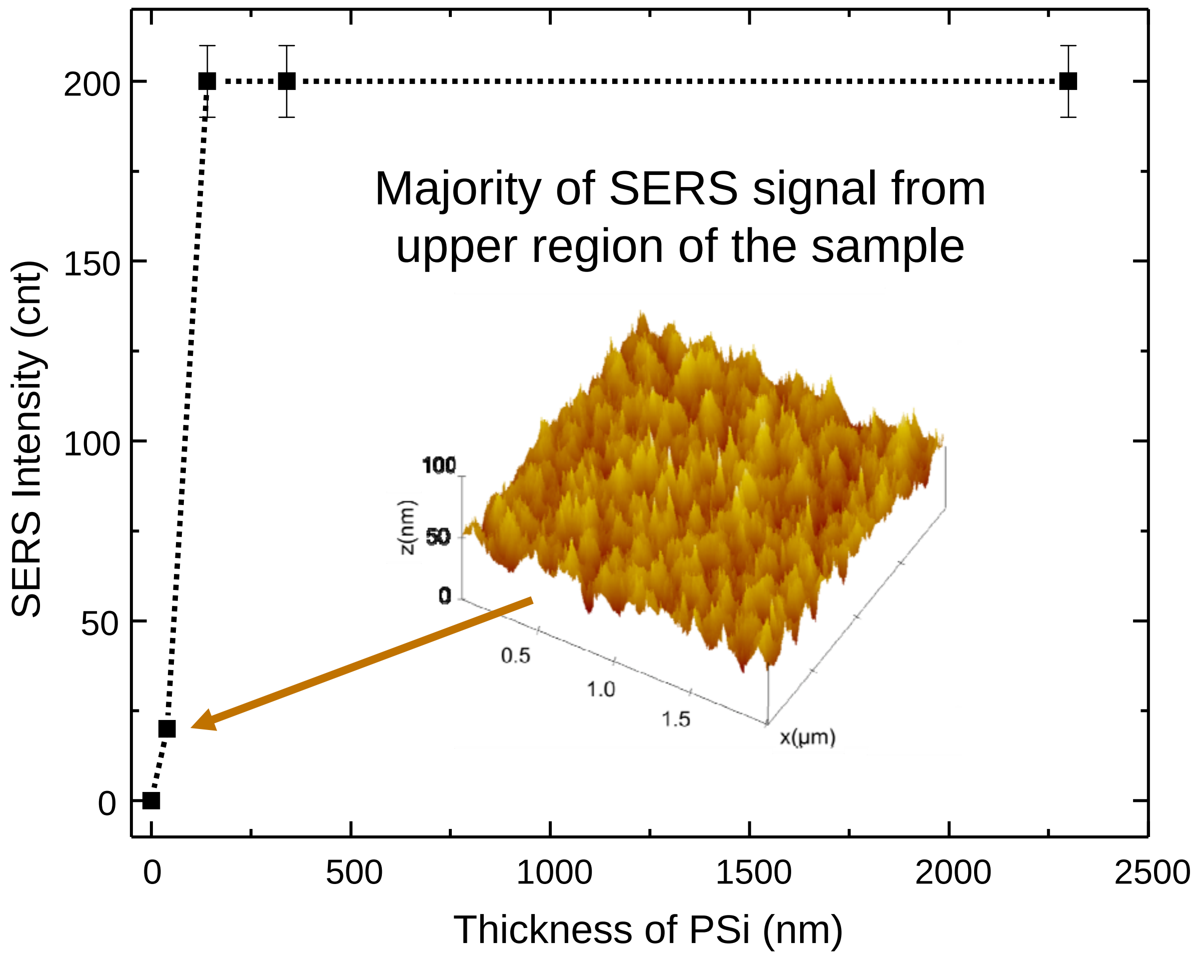
SERS Measurement

Sensitivity < 1μM, Estimated SERS enhancement ≈ 10^5



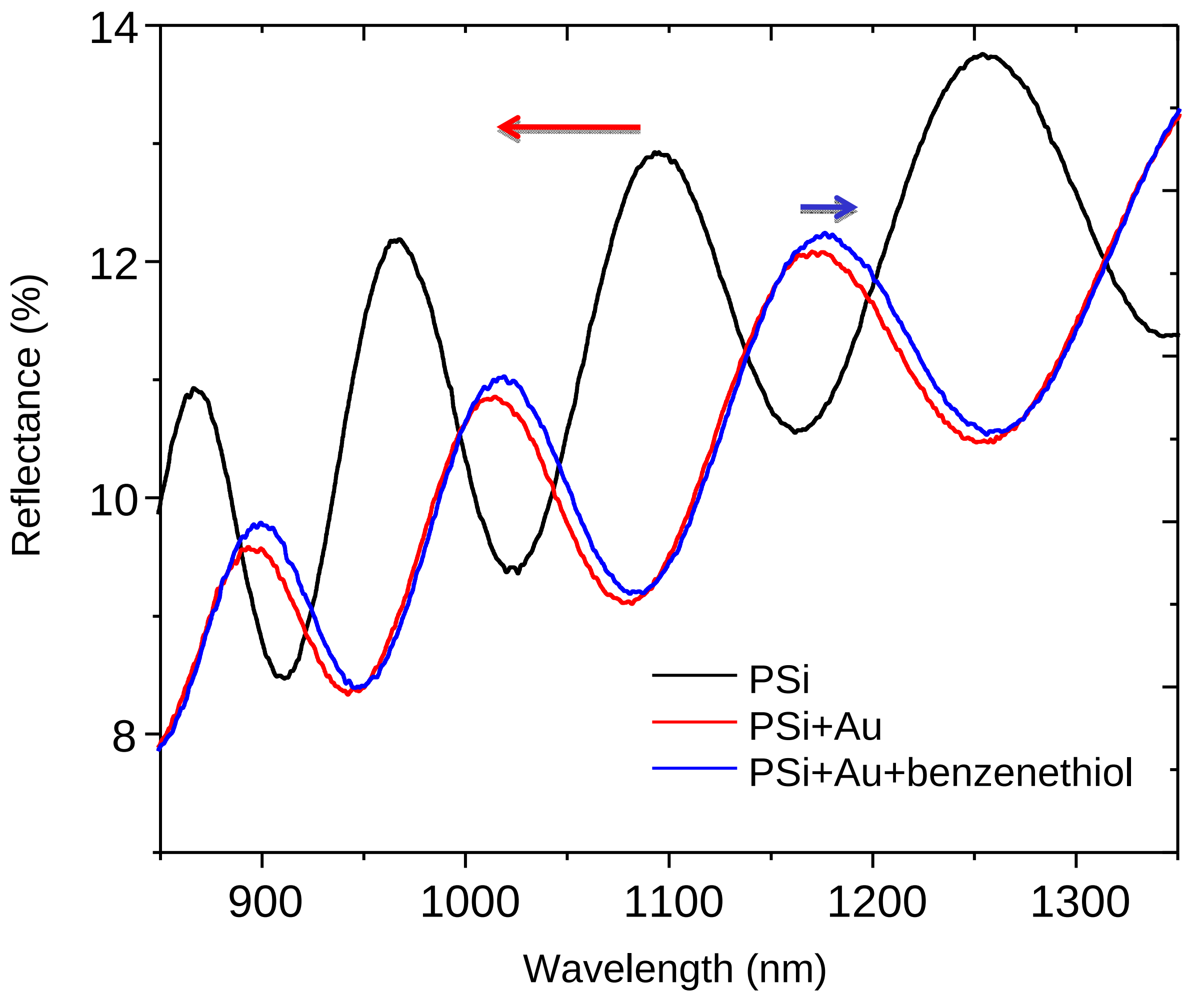
VANDERBILT
SCHOOL OF ENGINEERING

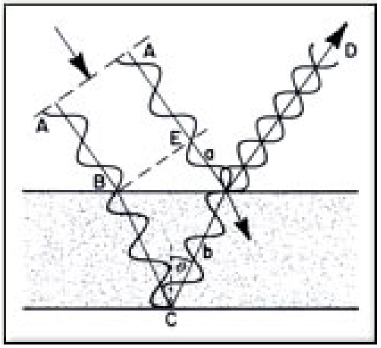
Thickness Dependence of SERS



Reflectance Measurements

Sensitivity ≈ 400nm/RIU





http://www.webexhibits.org/causesofcolor/15.html

Reflectance shifts due to changes in effective refractive index of PSi film

Summary

- Nanoscale porous materials have advantages of large surface area and size-selective filtering
- Porous silicon waveguides and diffraction gratings offer highly sensitive platforms for analyte detection
  - Detection sensitivity depends on pore size, biomolecule size, and probe molecule surface coverage
  - New DIPS imprinting technique offers simple, economical platform for creating optical structures
- Dual mode sensor platform with gold nanoparticles enables SERS and refractive index sensing